Determination of cadmium in used engine oil, gasoline and diesel by electrothermal atomic absorption spectrometry using magnetic ionic liquid-based dispersive liquid-liquid microextraction

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Abstract

In this study, a sensitive and matrix-effect free analytical method for Cd determination in engine oils and fuel samples by dispersive liquid-liquid microextraction with electrothermal atomic absorption spectrometry has been successfully developed. The extractant solvent used for the microextraction procedure was a magnetic ionic liquid (MIL) (i.e., bis(1-ethyl-3-methylimidazolium) tetrathiocyanatocobaltate (II) $[Emim]_2[Co(NCS)_4]$), which presents a paramagnetic property, and allows an easy phase separation using a magnet. In order to eliminate the well-known drawbacks of direct introduction of MIL in the graphite furnace, a back-extraction procedure was performed to transfer the analyte into an aqueous phase. The main experimental factors affecting the extraction of Cd (i.e., amount of sample and MIL, extraction and back-extraction time and concentration and amount of nitric acid) were optimized using a multivariate analysis consisting in two steps: a Plackett-Burman design followed by a circumscribed central composite design. Under optimum conditions (i.e., amount of sample: 6.2 g; amount of MIL: 119 mg; extraction time: 1 min; amount of nitric acid: 200 mg; nitric acid concentration: 1 mol L^{-1} and back-extraction time: 1 min.), the proposed analytical method was validated and successfully used to analyze three real-world samples (i.e., used engine oil, gasoline and diesel). The three samples were spiked at two levels (i.e., 10 and 20 µg kg^{-1} of Cd for used engine oil and 1 and 3 µg kg^{-1} of Cd for gasoline and diesel). RSD and recovery values were within the range of 6-11 % and 96-105 %, respectively.

1. Introduction

The determination of metal levels in fuel products and used engine oils is of prime importance to the industrial machinery, transport and utility industries since it can lead to several detrimental effects for both automobile engine as well as the environment [1, 2]. From engineering point of view, the presence of trace elements in fuel products can dramatically decrease engine performance by negatively impacting the combustion process [3]. In addition, the quantitative determination of metals in used engine oils is performed to monitor and diagnoses engine wear, in order to attain preventive maintenance actions [4]. From environmental point of view, undesirable metallic elements generate air pollution due to their release into the atmosphere by the fuel combustion [5]. Furthermore, used engine oil is generally spilled on the land but this oil can be transferred rapidly to aquatic environments by rain and runoff waters, affecting adversely the environmental health [6]. Despite the numerous toxic elements that can be present in engine and fuel samples, cadmium is considered one of ten chemicals of major health concern by the World Health Organization, with a wide range of toxicity and long elimination half-life [7]. In this scenario, it is clear that the development of analytical methods for determination of cadmium is required for the quality control of fuel products or the proper management of engine oil waste.

In the last decade, most analytical methods reported in the literature for the determination and quantification of contaminants in these samples are based on atomic spectrometric techniques such as flame atomic absorption spectrometry (FAAS) [8-10], electrothermal atomic absorption spectrometry (ETAAS) [11-13], inductively coupled plasma-based techniques, which include optical emission spectrometry (ICP OES) [14-16] and mass spectrometry (ICP-MS) [2, 5]. Without a doubt, FAAS and ICP OES are the two most employed techniques for elemental analysis in fuel products and oil samples. However, the sensitivity achieved is limited when low-ppb determination is required, being ETAAS and ICP-MS the best options for this kind of applications. Particularly, ETAAS can be considered a suitable analytical technique for this purpose because of its wide availability and good sensitivity, in contrast to ICP-MS since its instrumentation cost.

Despite its broad application, the direct determination of ultra-trace levels of cadmium in organic sample by ETAAS is not without problems. On one hand, the requirement of the use of organometallic standards increases the cost of the analysis significantly. On the other hand, fuel samples tend to distribute along the length of the graphite tube owing to

their lower surface tension and good wetting ability, thereby leading to loss of sensitivity [17], and lubricating oils cause inefficient injection into the graphite tube due to their high viscosity. In addition, for both samples ashing temperatures and time must be chosen carefully to avoid residual organic matter or smoke interfering in the analysis. Another problem is that the sensitivity of ETAAS is compromised when samples with complex matrix are analyzed. In order to reach enough sensitivity in the determination of Cd in these samples, a preconcentration step is often required before the detection by ETAAS [18]. In the field of elemental analysis, microextraction techniques, particularly dispersive liquid-liquid microextraction (DLLME), have been extensively used since their advantages, including speed and ease of use, low cost and high enrichment factors. One of the improvements on conventional DLLME involves the use of ionic liquids (IL) due to their remarkable properties and higher enrichment factor in comparison with conventional solvents [19]. Recently, a novel subclass of ionic liquid named magnetic ionic liquids (MIL) has been presented as new extractant solvents for liquid-phase microextraction of metals from different matrices [20-23]. The paramagnetic properties of MILs are induced by the anion, the cation or both, presented in their structure and possess similar physicochemical properties to conventional ionic liquids but, additionally, show response under the application of an external magnetic field [24, 25]. The resulting paramagnetic behavior of these solvents facilitates their manipulation providing remarkable advantages. For example, time-consuming centrifugation step is avoided in dispersive liquid-liquid microextraction since phase separation is accomplished using a magnet [24]. In contrast, the quantification by injecting the MIL directly into the graphite furnace should, to the extent possible, be discouraged. An efficient and elegant way to circumvent this is to combine extraction with back-extraction procedure, that is, to transfer the analyte into an aqueous phase which is a more compatible for ETAAS measurements.

Therefore, the aim of the present work was to develop a sensitive and matrix-effect free analytical method for Cd determination in engine oils and fuel samples by ETAAS. The new method synergistically combines DLLME technique and the MIL bis(1-ethyl-3-methylimidazolium) tetrathiocyanatocobaltate (II) $[Emim]_2[Co(NCS)_4]$ for the efficient extraction and preconcentration of Cd.

2. Experimental

2.1. Instrumentation

An atomic absorption spectrometer model 600 (PerkinElmer, Shelton, USA), furnished with a transversely heated graphite atomizer and a Zeeman-effect background correction device, was used. Pyrolytic graphite platforms inserted into pyrolytically coated tubes were obtained from the same manufacturer (reference B050-4033). The inert gas was argon flowing at 250 mL min^{-1} during all the stages except atomization, when the flow was stopped. The radiation source was a cadmium hollow cathode lamp (PerkinElmer) operating at 10 mA. Integrated absorbance was exclusively used as the analytical signal. The instrumental parameters as well as the optimized temperature program are summarized in **Table 1**.

2.2. Reagents and samples

Cadmium standard solutions were prepared from multi elemental stock solution (CONOSTAN, SCP Science, Baie D'Urfé, Canada). Appropriate working standard solutions were obtained by dilution. For extraction condition optimization, a 2 μg kg^{-1} Cd standard solution was used. The solvent used for this calibration standard was kerosene (Panreac, Barcelona, Spain; boiling range 190-250 °C) and the blank calibration standard was also prepared using this solvent. For back-extraction procedure, HNO_3 (65%) from Panreac was employed to prepare 1 mol L^{-1} of HNO_3 in distilled deionized water (18 MΩ cm resistivity). Solution containing 500 mg L^{-1} of Pd was used as a matrix modifier and it was prepared from mono elemental stock solution (Merck, Darmstadt, Germany). The MIL $[Emim]_2[Co(NCS)_4]$ was supplied by Io-Li-Tec (Ionic Liquid Technologies, Heilbronn, Germany).

The used engine oil was obtained from a local car workshop close to the University of Alicante. Used lubricating oils were drained from a car engine during a routine service at a garage after usage at a certain mileage (i.e., 20,000 km). It was stored in amber glass flasks at 4 ºC. The engine oil was gravimetrically diluted (1:25) with kerosene (Panreac) in order to decrease their viscosity and to determinate the Cd concentration within the linear range evaluated.

Diesel and gasoline samples were purchased at a petrol station close to the University of Alicante and were stored in polyethylene terephthalate (PET) containers and kept in the

refrigerator until analyzed. Before performing the analysis, the samples were allowed to reach room temperature and they were analyzed without dilution.

2.3. General procedure

For the analyte extraction, a sample amount of 6.2 g was placed in a 15 mL glass tube along with MIL amount of 119 mg. The mixture was shaken for 1 min with a vortex stirrer. Subsequently, a magnet was used to separate the MIL phase from the organic phase. Finally, a 40 mg of the extractant (i.e., MIL phase) was added to 200 mg of 1 mol L^{-1} HNO_3 solution in order to perform the back-extraction of the analyte from the MIL phase to aqueous phase, shaking by vortex for 1 minute. A volume of 10 μL of the aqueous phase containing the analyte and 10 μL of matrix modifier were injected into the graphite furnace of ETAAS instrument for Cd determination (**Figure 1**).

2.4. Data processing

A multivariate optimization strategy was performed to determine the optimum extraction conditions. Statgraphics statistical computer package "Statgraphics Centurion XVI" (Warrenton, VA, USA) was used to construct the experimental design matrices and evaluate the results.

3. Results

3.1. Design of experiment

Generally, two steps are needed for multivariate optimization: a screening of main effects of the selected factors and a response optimization. In the screening approach, a Plackett-Burman factorial design was employed. This design allows the evaluation of the effect in the absorbance of different factors, distinguishing between significant and non-significant ones. Optimal levels of significant factors were obtained with a circumscribed central composite design (CCCD). This design allows to predict the more appropriate experimental conditions to achieve the maximum absorbance.

3.1.1. Screening step

In order to obtain the highest response, the effect of different factors, amount of MIL and sample, extraction and back-extraction time, and concentration and amount of nitric acid solution were selected to optimize the absorbance of Cd by multivariate approach. The

factors and their low (-) and high (+) levels, are described in **Table 2**. A Plackett-Burman design was used to construct the matrix of experiments, including six factors studied in eight runs. The Cd concentration of 2 µg kg^{-1} was kept constant for all experiments. The results of the design are visualized using a Pareto chart of the standardized effect in **Figure 2**.

The length of the bars shown is proportional to the significance of the estimated main factors that affect the absorbance of Cd. Bars extending beyond the vertical line indicate statistically significant factors at 95% probability. Interpretation of the graphic study presented in **Figure 2** leads to conclude that only the two factors (i.e., amount of MIL and sample) are statistically influent in the Cd absorbance. The sign (i.e., positive) related to those factors indicates that an increase of Cd absorbance is obtained with higher amount of MIL and sample.

All the remaining experimental factors have no significant influence on the Cd absorbance and therefore they are not statistically significant. Levels of concentration and amount of nitic acid solution were set at their higher level (i.e., 200 mg of nitric acid 1 mol L^{-1}), and extraction and back-extraction time were fixed at their lower level for subsequent extractions (i.e., 1 minute in both cases).

3.1.2. Optimization step

After screening the factors that have no significant effect on the Cd absorbance, the remaining two factors, amount of MIL and sample were optimized to provide the maximum absorbance. On a circumscribed central composite design, 12 new experiments were carried out to optimize these factors. **Table 3** shows the different level values chosen in the CCCD. This experimental design involves five levels for each factor: a low level (-1), a central level (0), a high level (+1), and two star points located at $\pm\alpha$ ($\alpha = 1.41$). The result obtained in this study is shown in **Figure 3** as response surface. As observed from **Figure 3**, amount of sample reaches an optimum value for extraction of Cd at 6.2 g. Increasing the amount of sample in DLLME leads to an increase in the total amount of analyte presents in the solution. Consequently, a greater amount of analyte was transferred to the extractant solvent. However, the amount of sample has a great influence in the extraction efficiency since the highest factor in the CCCD matrix (i.e., 6.6 g of sample) prevent the vortex formation, worsening the dispersion of the MIL. The amount of MIL has also a direct influence on the DLLME, reaching a maximum at 119 mg. An

increase in the amount of MIL leads to an increase in the final volume of organic phase in which analytes are extracted. In contrast, an excessive amount of MIL could lead to a dilution effect, thus decreasing the preconcentration factor.

In summary, the DLLME experimental conditions selected were: Amount of sample: 6.2 g; amount of MIL: 119 mg; extraction time: 1 min; amount of nitric acid solution: 200 mg; nitric acid concentration: 1 mol L^{-1} and back-extraction time: 1 min.

3.2. Validation of the method

Table 4 summarizes the analytical performance of the proposed method, under optimum experimental conditions. The enrichment factor obtained, calculated as the slope between calibration curves with and without DLLME, was 220. The working range using DLLME procedure was establish from 1 to 5 µg kg^{-1} and the correlation coefficients (r) was 0.998, showing good linearity. The reproducibility of the measurements was estimated by analyzing 10 microextraction experiments at Cd concentration of 2 and 4 µg kg^{-1} and each extract being measured in duplicate. The relative standard deviations obtained were 9.6 and 10 %, respectively. According to Eurachem guidelines [26], limit of quantification (LOQ) is calculated by most conventions to be the analyte concentration corresponding to the obtained standard deviation (i.e., determined by 10 consecutive measurements of the blank) at low levels multiplied by a factor k. The IUPAC default value for k is 10 [27]. Limit of detection (LOD) is calculated analogously to the LOQ. However, the IUPAC default value for k is 3 [27]. The LOD and LOQ values for Cd were 84 and 280 ng kg^{-1}, respectively.

To the best of our knowledge, the **Table 5** summarizes the lowest LOD values obtained for Cd in fuel samples for different atomic techniques. The comparison of the analytical performance of the proposed method with previously reported methods with different atomic spectrometric techniques shows that a powerful alternative method has been developed. Summarizing, the application of the MIL-DLLME procedure can enhance sensitivity of the ETAAS technique obtaining LOD value slightly higher in comparison to that obtained with ICP-MS. But this is not the only advantage of the proposed method. In this work, the cadmium has been extracted from a very problematic solvent (i.e., fuel samples and engine oil) to a more compatible solvent (i.e., aqueous phase).

3.3. Analysis of real-world samples

Negative matrix effects were found when analyzing three different real-world samples (i.e., used lubricating oil, gasoline and diesel). Therefore, standard addition calibration was employed to assess the applicability of the proposed analytical method under optimized extraction conditions for the three samples (**Table 6**). The three samples were spiked at two levels (i.e., 10 and 20 µg kg^{-1} of Cd for used engine oil and 1 and 3 µg kg^{-1} of Cd for gasoline and diesel). Trueness of results obtained with the proposed method was verified by evaluating recovery values of Cd from each spiked sample. Obtained recovery values were within the range of 96-105 %. Precision of these results was within 6-11%. Both measures indicated that there was a relatively no influence of the analyzed sample matrix, while the proposed analytical system provided fairly accurate (precise and true) concentrations of Cd.

4. Conclusions

For the first time, MIL-DLLME and back-extraction procedures have been successfully combined with ETAAS to determine Cd in used engine oil, gasoline and diesel. This combination synergistically exploits the advantages of environmentally friendly miniaturized sample preparation with the fast (i.e., less than 3 minutes), affordable and sensitive determination of cadmium. The proposed method avoids the use of time-consuming mineralization by microwave digestion and it solves all problems about organic matrix in ETAAS since Cd determination is performed in aqueous media. Moreover, the high enrichment factor obtained using MIL-DLLME, together with the sensitivity of ETAAS, results in an extremely sensitive analytical procedure with LOQ value comparable with that achieved by ICP-MS [5].

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Tables

Table 1. Instrumental parameters and furnace heating program.

Instrumental parameters	Cadmium
Lamp current (mA)	10 (HCL)
Wavelength (nm)	228.8
Bandwidth (nm)	0.7
Atomizer type	Platform
Injected sample volume (µL)	10
Chemical modifier	Palladium nitrate (500 mg L^{-1})
Injected chemical modifier volume (µL)	10
Background correction	Zeeman

Furnace heating program

Step	Temperature (ºC)	Ramp time (s)	Hold time (s)
1: Dry I	110	5	20
2: Dry II	300	5	30
3: Pyrolysis	500	15	20
4: Atomization[a,b]	1500	0	4
5: Clean	2600	1	5

[a]Stopped internal gas flow
[b]Reading stage

Table 2. Experimental factors and levels of the Plackett-Burman design.

Experimental factor	Level	
	Low (-)	High (+)
Amount of sample (g)	3	6
Amount of MIL (mg)	60	120
Extraction time (min)	1	3
Amount of nitric acid solution (mg)	100	200
Nitric acid concentration (M)	0.5	1.0
Back-extraction time (min)	1	3

Table 3. Experimental factors and levels of the circumscribed central composite design.

Experimental factor	Level			Star points (α=1.41)	
	Low (-)	Central (0)	High (+)	-α	-α
Amount of sample (g)	3	4.5	6	2.4	6.6
Amount of MIL (mg)	60	90	120	47.6	132.4

Table 4. Analytical performance of the proposed method.

Analyte	Linear range (µg kg^{-1})	r[a]	RSD[b] (%) 2 µg kg^{-1}	RSD[b] (%) 4 µg kg^{-1}	LOD (ng kg^{-1})	LOQ (ng kg^{-1})	EF[c]
Cd	0-5	0.998	9.6	10	84	280	220

[a]Correlation coefficient. Number of calibration points: 6.
[b]Mean value for 10 replicated analysis, being measured in duplicate of 2 and 4 µg kg^{-1} spiked solution.
[c]Enrichment factor: calculated as slope ratio between calibration curves with and without MIL-DLLME.

Table 5. Comparison of the developed method with previously reported methods with different atomic spectrometric techniques to determine cadmium in fuel samples.

Technique	Procedure	Time (min)	EF	LOD	Reference
FAAS	Molecularly imprinted polymer	Sorption time: 4 min Desorption time: 50 min	184	0.09 µg L^{-1}	[10]
ETV	Microemulsion	No indicated	-	0.5 µg kg^{-1}	[13]
ICP-OES	Solid-phase extraction	4	60	0.48 µg L^{-1}	[16]
ICP-MS	Extraction induced by microemulsion breaking	0.3-0.6	1.74	0.06 µg L^{-1}	[5]
ETV	MIL-DLLME	2	220	0.084 µg kg^{-1}	This work

Table 6. Spiked and found concentrations and recovery values obtained in the determination of Cd in different real-world samples.

Sample	Spiked value (µg kg^{-1})	Found value (µg kg^{-1})	Recovery (%)
Engine oil	-	35±5	-
	10	46±5	105±6
	20	54±5	96±7
Diesel	-	0.90±0.05	-
	1.2	2.10±0.07	102±10
	3.2	4.03±0.17	99±6
Gasoline	-	0.68±0.07	-
	1.1	1.81±0.09	103±11
	2.9	3.55±0.11	97±6

Figures

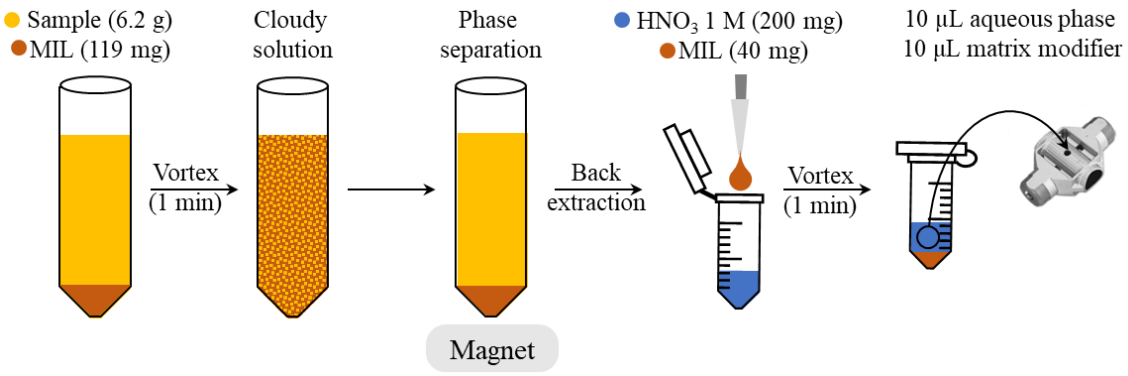

Figure 1. Scheme of the analytical procedure for Cd quantification.

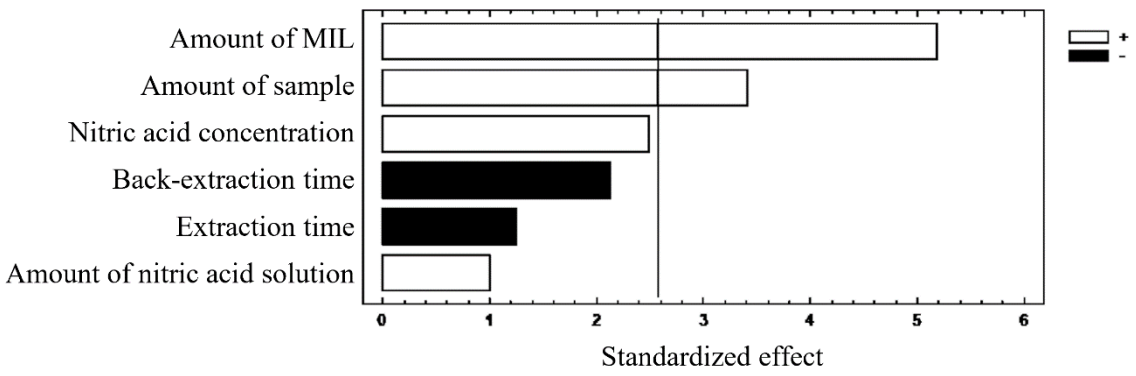

Figure 2. Pareto chart obtained in the screening study of the experimental factors affecting the MIL-DLLME in the Cd absorbance.

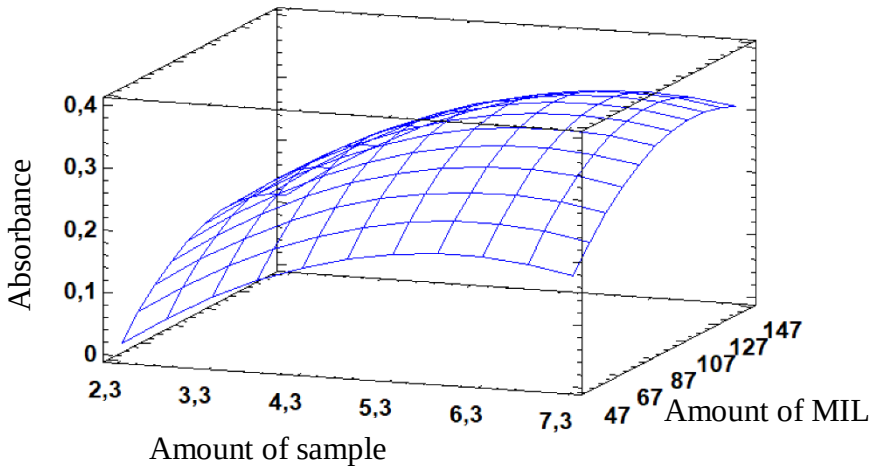

Figure 3. Response surface from circumscribed central composite design.